NOTE

Indian J. Phys. **71A** (1), 83–87 (1997)

IJP A
— an international journal

Magnetic study of gadolinium-iron-transition metal mixed oxides

A N Thakur, K Gaur, M A Khan and H B Lal

Department of Physics, University of Gorakhpur,
Gorakhpur-273 009, India

Received 11 July 1996, accepted 15 July 1996

Abstract : The compounds of Gadolinium-iron-transition metal mixed oxides of the type $GdFeTO_4$ have been prepared by solid state reaction technique and characterised by XRD pattern. The molar magnetic susceptibility (χ_M) of the powdered sample have been reported in the temperature range 300 to 1100 K. All the materials show a typical ferri-magnetic behaviour and χ_M vs T plot can be expressed by standard relations. The slope of asymptotic line to the curve yields and average magneton number which indicates that material is perfectly ionic. The transition metal ions are Fe^{2+} and Fe^{3+} in $GdFe_2O_4$, Fe^{2+} and Cr^{3+} in $GdFeCrO_4$, Fe^{2+} and Mn^{3+} in $GdFeMnO_4$, Fe^{3+} and CO^{2+} in $GdFeCoO_4$ and Fe^{3+} and Ni^{2+} in $GdFeNiO_4$.

Keywords : Magnetic susceptibility, gadolinium-iron-transition metal mixed oxides

PACS Nos. : 07.55.–w, 75.30.Cr

Rare-earth and transition metal elements are characterised by their unfilled $4f$ and $3d$ orbitals. Due to this reason the compounds of rare-earth and transition metal yield variety of materials with interesting and useful magnetic properties, which have not only enriched our understanding but have found numerous applications [1–3]. We have prepared a series of rare-earth transition metal mixed compounds with a general formula of $RETT'O_4$, where RE stands for rare-earth, T and T' for transition metals. This paper reports our study regarding the magnetic susceptibility of one of the compounds of this series namely $GdFeTO_4$. Only limited studies have been reported on this compounds. The material of this series that has been studied is $GdFe_2O_4$. These studies are related with low temperature phase transition [4,5], neutron diffraction and magnetic properties [6,7]. Mössbauer studies [8,9] and dielectric properties [10]. No study on any other compound of this series has been reported in the literature so far.

The starting materials for the preparation of these compounds were Gd_2O_3, Fe_2O_3 and oxides Cr_2O_3, NiO, CoO and MnO_2 which are 99.9% pure. The stoichiometric amount

of these oxides were mixed and heated in a silica crucible for 50 hrs at a temperature of 1400 K. In this process, the mixture was subjected to intermediate grinding and the final product was cooled down slowly. The prepared compounds undergo the following solid state reactions :

$$2\,Gd_2O_3 + 4\,Fe_2O_3 \xrightarrow[Air]{1400\ K} 4\,GdFe_2O_4 + O_2,$$

$$2\,Gd_2O_3 + 2\,Fe_2O_3 + 2\,Cr_2O_3 \xrightarrow[Air]{1400\ K} 4\,GdFeCrO_4 + O_2,$$

$$Gd_2O_3 + Fe_2O_3 + 2\,MnO_2 \xrightarrow[Air]{1400\ K} 2\,GdFeMnO_4 + O_2,$$

$$Gd_2O_3 + Fe_2O_3 + 2\,CoO \xrightarrow[Air]{1400\ K} 2\,GdFeCoO_4,$$

$$Gd_2O_3 + Fe_2O_3 + 2\,NiO \xrightarrow[Air]{1400\ K} 2\,GdFeNiO_4.$$

The weight loss corresponding to loss of oxygen on the right hand side of the reactions was observed in all cases except in $GdFeMnO_4$. In this case, the observed loss was slightly less than expected. The details are described elsewhere [11].

To get the confirmation regarding the complete formation of the prepared compounds, X-ray diffraction study has been carried out at room temperature using CuK_α radiation ($\lambda = 0.15418$ nm). From X-ray diffraction pattern, d_{hkl} values have been evaluated using the relation

$$d_{hkl} = \frac{0.15418}{2 \sin \theta} \tag{1}$$

From these values of d_{hkl}, structure of the compounds were resolved using usual procedure All the peaks have been identified and assigned proper hkl values. This confirms that prepared compounds are in single phase. All the compounds have been found to have orthorhombic unit cell with unit cell parameters a_0, b_0 and c_0 as given in Table 1.

Table 1. Structural parameters of the studied $GFeTO_4$ compounds.

Compound	Lattice parameters (nm)			Unit cell volume	Calculated density
	a_0	b_0	c_0	$m^3 \times 10^{28}$	$Kg\ m^{-3} \times 10^{-3}$
$GdFe_2O_4$	0.6242	0.7366	0 8836	4.0627	5.44
$GdFeCrO_4$	0 6340	0 7282	0 8858	4 0896	5.34
$GdFeMnO_4$	0 6274	0.7386	0 8856	4 1039	5.37
$GdFeCoO_4$	0 6286	0 7416	0 8924	4.1601	5.36
$GdFeNiO_4$	0.6296	0.7386	0.8878	4.1285	5.40

Magnetic susceptibility measurements were done on powdered samples using Faraday's method [11,12].$Gd_2(WO_4)_3$ has been used for standardisation.

The molar magnetic susceptibility (χ_M) of all the compounds was measured in both heating and cooling cycles. No hysteresis was observed in χ_M and values were found to be almost same in both heating and cooling cycles. However, a small weight loss was noticed in heating cycle probably due to presence of moisture. The results are presented in Figure 1 as χ_M^{-1} *vs* T plots. It is seen from this figure that nature of all these plots are essentially

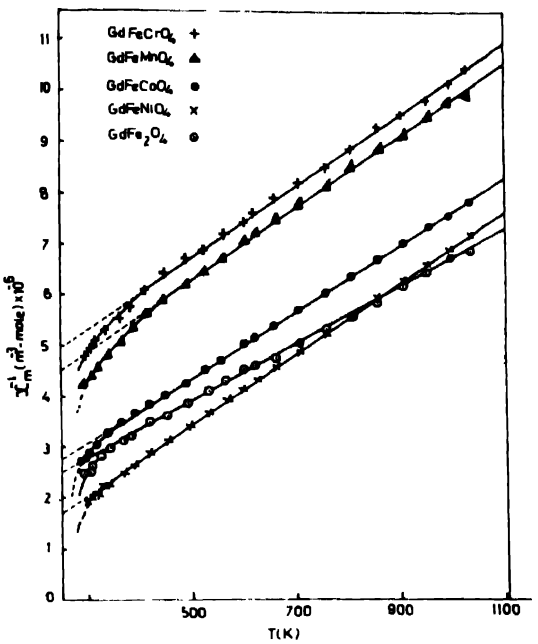

Figure 1. Plot of inverse of molar magnetic susceptibility (χ_M^{-1}) against absolute temperature (T) for studied compounds.

similar. In general, χ_M^{-1} *vs* T plots are linear at higher side of temperature. However, there is systematic trend of experimental points towards temperature axis at lower side of temperature. The curves are similar to a standard ferrimagnetic material and systematic downward trend is due to the onset of short range magnetic interaction at lower side of temperature. We have tried to fit the experimental points to the standard equation of ferrimagnetism given below by choosing the suitable parameters :

$$\frac{1}{\chi_M} \quad \frac{T-\theta_a}{C_M} \quad \frac{\theta_b^2}{C_M(T-\theta)}, \tag{2}$$

$\overline{C}_M$ is the average value of Curie constant, θ_a is the asymptotic Curie temperature and θ_b and θ are parametric temperatures. These curves using eq. 2 are drawn by full line in respective χ_M^{-1} vs T plots. It is seen that experimental point can be well fitted by eq. 2 over wide temperature range. The values of $\overline{C}_M$, θ_a, θ_b and θ are given in Table 2. The ferrimagnetic Curie (or Neel) temperature have been evaluated using condition $T \to T_c$, $\chi_M^{-1} \to 0$. This gives

$$(T_c - \theta_a)(T_c - \theta) = \theta_b^2 \tag{3}$$

The real and positive value of T_c are meaningful and have been calculated using above relation. These values are also given in Table 2.

Table 2. Magnetic parameters of studied compounds.

Compound	θ_a (K)	θ (K)	θ_b (K)	T_c (K)	C_M $(mol^{-1}m^3K) \times 10^4$
$GdFe_2O_4$	–235	240	76	252	1.903
$GdFeCrO_4$	–580	249	97	260	1.466
$GdFeMnO_4$	–707	251	93	260	1.736
$GdFeCoO_4$	–330	253	96	268	1.763
$GdFeNiO_4$	–108	243	72	257	1.654

The compound $GdFeT'O_4$ contains only three types of magnetic ions Gd^{3+}, Fe^{3+} or Fe^{2+} and T'^{3+} or T'^{2+}. Thus at temperature much higher to T_c, the molar magnetic susceptibility of these compounds can be expressed by the relation

$$\chi_M = \frac{N\mu_\beta^2\mu_0}{3K}\left[\frac{P_1^2}{T-\theta_{a1}} + \frac{P_2^2}{T-\theta_{a2}} + \frac{P_3^2}{T-\theta_{a3}}\right], \tag{4}$$

where N is Avogadro number, μ_β is Bohr magneton, μ_0 the permeability constant, K is Boltzman constant, P_1, P_2 and P_3 are the magneton numbers of three types of magnetic ions respectively and θ_{a1}, θ_{a2} and θ_{a3} are paramagnetic Curie temperatures which takes into account the effect of various interaction. Assuming $\theta_{a1} = \theta_{a2} = \theta_{a3}$, we can write above equation as

$$\chi_M^{-1} = \frac{k(T-\theta_a)}{N\mu_\beta^2\mu_0\bar{P}^2},$$

where $$\bar{P}^2 = \frac{P_1^2 + P_2^2 + P_3^2}{3}$$

is the average effective magneton per ion.

Comparing this equation with asymptotic equation of the curve given by eq. 2, one gets

$$\theta = \theta_a \text{ and } \bar{C}_M = \frac{N\mu_\beta^2\mu_0\bar{P}^2}{k}$$

or

$$\bar{P} = \left[k\bar{C}_M / N\mu_\beta^2\mu_0\right]^{1/2} \tag{5}$$

The experimental value of $\bar{P}$ can be calculated from the evaluated value of $\bar{C}_M$. The theoretical values of P_1, P_2 and P_3 are known. Hence, one can obtain the theoretical values of $\bar{P}$. The experimental and theoretical values of $\bar{P}$ are given in Table 3 together with the magnetic ions used to obtain theoretical values of $\bar{P}$.

It is seen from this table that there is a good agreement between the theoretical and experimental values of $\bar{P}$. This indicates that all the studied compounds are essentially

ionic and magnetic states of the ions are as indicated in the second column of the Table 3. One can notice that in $GdFeCrO_4$ and $GdFeMnO_4$ compounds there exists Cr^{3+} and Mn^{3+}

Table 3. Magnetic ions and average effective magneton number per ion ($\bar{P}$).

Compound	Magnetic ions			Values of $\bar{P}$	
				Theo.	Expt.
$GdFe_2O_4$	Gd^{3+}	Fe^{3+}	Fe^{2+}	6.38	6.37
$GdFeCrO_4$	Gd^{3+}	Cr^{3+}	Fe^{2+}	5.83	5.59
$GdFeMnO_4$	Gd^{3+}	Mn^{3+}	Fe^{2+}	6.09	6.08
$GdFeCoO_4$	Gd^{3+}	Fe^{3+}	Co^{2+}	6.14	6.13
$GdFeNiO_4$	Gd^{3+}	Fe^{3+}	Ni^{2+}	5.95	5.94

ions and they substitute Fe^{3+} ions. This is quite reasonable in view of natural valency of these elements.

Acknowledgment

One of the authors (ANT) is thankful to CSIR, for financial assistance.

References

[1] R S Tebble and D J Crack *Magnetic Materials* (London : John Wiley) (1969)

[2] K J Standley Oxide *Magnetic Materials* (Oxford : Claender) (1972)

[3] E P Wohlfarth (Ed) *A Hand Book of Magnetically Ordered Magnetic Materials* Vols I and II and III (1982) (Amsterdam : North Holland) (1980)

[4] Y Nakagawa, M Imazumi, N Kimizuka and K Siratori *J. Phys. Soc. Jpn.* **47** 1369 (1979)

[5] M Tanaka, K Siratori and N Kimizuka *J. Phys. Soc. Jpn.* **53** 760 (1984)

[6] S Funasaki, Y Morii and H R Child *J. Appl. Phys.* (USA) **6** 4114 (1978)

[7] Y Nakagawa, F Kawaguchi, T Hayakawa, Y Xto, H Yamada, M Yoshida, F Fujii, H Takaguchi and Y Tsukuda *J. Appl. Phys.* (Japan) **27** 1572 (1988)

[8] M Tanaka, J A Kimitsu, N Kimizuka, I Sindo and K Siratori *Proc. Int. Conf. Ferrites* (Kyoto) 119 (1980)

[9] M Imazumi, Y Nakagawa, M Tanaka, N Kimizuka and K Siratori *J. Phys. Soc. Jpn.* **50** 438 (1981)

[10] A N Thakur, K Gaur and H B Lal *J. Mater. Sci. Lett.* **11** 496 (1992)

[11] A N Thakur *PhDThesis* (University of Gorakhpur, India) (1992)

[12] H B Lal and V Pratap *J. Mater Sci.* **17** 377 (1982)